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12. ABSTRACT (Maximum 200 words)

Low and high molecular weight polymers of heptafluorobutyl methacrylate, HFEM, were prepared for commercial evaluation by Bicron, an optical fiber manufacturer. Polymers were evaluated as low refractive index fiber cladding materials. Test results of Low MW polymer solutions gave excellent results. Higher MW polymers were prepared for cladding by melt co-extrusion. Corning Glass Corp. also expressed an interest in these cladding materials.

These results appear to be sufficiently unique that a search has been initiated to determine patentability of the soluble fluorocarbon acrylate, methacrylate and copolymer compositions for cladding use.

Our research resulted in identifying a radiation hard, low refractive index polymer, poly(heptafluorobutyl methacrylate), P(HFBM) as the best candidate for a novel cladding material. P(HFBM) has a refractive index of 1.387. When used to clad a styrene core, the theoretical light propagation efficiency is 50% greater than that of styrene a fiber core clad with PMMA, a common commercial cladding material.

These polymers will be the only commercial fluorocarbon acrylic cladding polymers available to U.S. manufacturers. Japanese optical fiber manufacturers produce fluorocarbon clad fibers but their polymers are not available to U.S. manufacturers. These polymers can fill an urgent need in the optical fiber market.

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FINAL TECHNICAL REPORT # 3

NOVEL, TRANSPARENT, RADIATION HARD,
LOW REFRACTIVE INDEX POLYMERS.

by:

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OPTICAL POLYMER RESEARCH, INC.

February 9, 1994

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I. ABSTRACT:

Low and high molecular weight polymers of heptafluorobutyl methacrylate, HFBM, were prepared for commercial evaluation by Bicron, an optical fiber manufacturer. Polymers were evaluated as low refractive index fiber cladding materials. Test results of Low MW polymer solutions gave excellent results. Higher MW polymers were prepared for cladding by melt co-extrusion. Corning Glass Corp. also expressed an interest in these cladding materials.

These results appear to be sufficiently unique that a search has been initiated to determine patentability of the soluble fluorocarbon acrylate, methacrylate and copolymer compositions for cladding use.

Our research resulted in identifying a radiation hard, low refractive index polymer, poly(heptafluorobutyl methacrylate), P(HFBM) as the best candidate for a novel cladding material. P(HFBM) has a refractive index of 1.387. When used to clad a styrene core, the theoretical light propagation efficiency is 50% greater than that of styrene a fiber core clad with PMMA, a common commercial cladding material.

These polymers will be the only commercial fluorocarbon acrylic cladding polymers available U.S. manufacturers. Japanese optical fiber manufacturers produce fluorocarbon clad fibers but their polymers are not available to U.S. manufacturers.

These Phase I results indicate that we can fill an urgent need in the optical fiber market.

II. INTRODUCTION.

Plastic Optical Fiber (POF) Technology is a rapidly growing industry world-wide, especially in the U.S., Japan and Europe. It is our understanding that at the present time there are no low refractive index, fluorocarbon cladding polymers available in the U.S. However, fluoropolymer clad poly(methylmethacrylate) is produced by Mitsubishi, a Japanese manufacturer, but the fluoropolymer cladding material is not available to POF manufacturers in the U.S. (See appendix A letter from Bicron)

POFs as well as silica fibers, are generally composed of two or more materials: a light carrying core having a higher refractive index than an outer, transparent cladding material. The low refractive index cladding

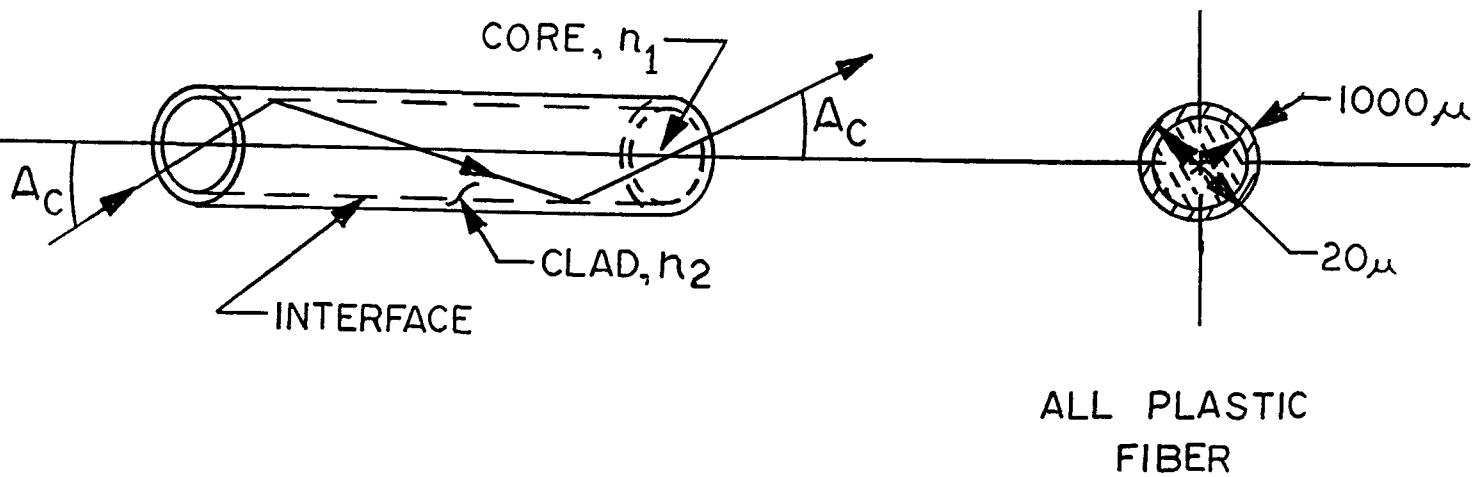
material improves the light carrying ability or efficiency of the fiber by preventing the escape of light from the core. The larger the difference in the refractive index between the core and outer coating, the greater the luminous properties of the fiber.

Figure 1 depicts a cylindrical section of an optical fiber showing a core of refractive index n_1 and a cladding material of n_2 . A light ray is shown entering the end of the fiber at angle, A_C . Light entering the fiber that exceeds angle, A_C , will penetrate the surface of the core and its light carrying ability will be lost. Angle, A_C , called the critical angle may be calculated from the respective refractive indices of the core and cladding material as $[n_1^2 - n_2^2]^{1/2} = N.A.$, where N.A. is the numerical aperture and the $\sin^{-1} N.A.$ is the critical angle, A_C . The cone of light entering the fiber is the acceptance angle, $2 \times A_C$. Thus, the larger the difference in the refractive index of the core versus the cladding material, the greater the light gathering and propagation efficiency.

In arriving at a suitable polymer for cladding an optical fiber it is readily apparent, from a summation of the atomic contribution to molar refraction of organic compounds that compounds containing a maximum amount of fluorine would yield the lowest attainable refractive index. For example, fluorine has a molar refraction of 0.81 and hydrogen 1.028. From this type of calculation one would assume that the commercially available polyfluoro-vinyl polymers would be the polymers of choice for low refractive index cladding. However, it has been found that the commercially available fluoropolymers in general have high scattering losses. These losses are generally attributable to polymer crystallinity. For example, semi-crystalline fluoropolymers are generally translucent to opaque solids with scattering losses near 10^6 dB/km. Similar to crystal scattering, particulate inclusions (impurities) are also a contributing factor to cladding losses.(1)

In addition to these unwanted factors, most, if not all, commercial fluoropolymers have softening points well above commercial core materials and have limited solubilities at required operating temperatures for solution coating. This means that the fluorovinyl polymers cannot be applied by heat processing or by solution coating.

FIGURE 1: Schematic Drawing of a Plastic Optical Fiber



III. POTENTIAL COMMERCIAL OPPORTUNITY.

There is a continuing and expanding need for optical fibers used in detectors or probes exposed to high energy radiation. The process by which this detection takes place is termed scintillation. Detection of a radioactive particle is made by means of excitation of an aromatic ring in the core of the POF (styrene). The particle excites the pi electrons in the aromatic ring. When these electrons relax to the ground state, a photon is released at a wavelength of 280-320nm. This photon is absorbed by a fluorescent dye in the fiber core and reemitted at a longer wavelength which permits detection by a photomultiplier.

Such fibers may be exposed to high doses of ionizing radiation, as much as 10 MRAD.

The most important use for low refractive index cladding polymers is in the manufacture of more efficient general purpose optical fibers, both POF's and silica core fibers. The general hydrophobicity of fluorocarbon polymers should be advantageous for glass fibers since they are particularly sensitive to the detrimental effects of moisture absorption.

IV. TECHNICAL OBJECTIVES.

There is a vital need for optical fiber cladding materials with the following characteristics:

- a. Low refractive index.
- b. Non-crystalline and transparent.
- c. Low temperature processing.
- d. Optical radiation hardness.

The object of this Phase I project was to synthesize small batches of homo and copolymers of fluorinated methacrylate monomers, to characterize the performance of these polymers and to select one polymer for commercial evaluation.

V. DISCUSSION.

In earlier research (2), carried out at the U. of Florida with the cooperation of Optical Polymer Research, Inc., it was found that the polymers made from acrylate esters of fluorocarbon alcohols have a high degree of transparency and have refractive indeces that decrease with increasing

fluorine content. In addition, these polymers meet all of the objectives outlined in IV, above.

Based on this work, polymers and copolymers of heptafluorobutyl methacrylate, HFBM and hexafluorobutyl methacrylate, HxFBM were chosen for further investigation.

A. Polymers and copolymers of HFBM and HxFBM.

1. Bulk polymerized polymers of HFBM and HxFBM.

These polymers were prepared by free radical initiation of degassed, inhibitor free monomers in polypropylene tubes under nitrogen. These polymers were used in all radiation and mechanical studies. The polymers are optically clear, solids that are not soluble in common solvents but swell in excess of 100% in simple solvents such as acetone. Although this would normally suggest that the polymers are cross-linked it was subsequently found that polymerization-controlled low molecular weight polymers of HFBM are soluble in some common solvents.

Polymers and co-polymers of HFBM and HxFBM, prepared by bulk polymerization, containing 25, 50, 75 and 100% of the respective monomers show the expected refractive index changes with composition as in Figure 2.

2. Soluble Polymers of HFBM.

As noted above bulk polymerization of HFBM yields high molecular weight polymers that are insoluble in solvents that are suitable for solution coating of optical fibers. However, lower molecular weight soluble polymers were produced by the addition of trace amounts of a chain growth regulator, dodecyl mercaptan, (DSH). Bulk polymerization of HFBM in the presence of

0.01 mole % of DHS produced polymers that are soluble in a solvent that appears to be unique for the dissolution of HFBM polymers, 2,2,2-trifluoroethyl acetate (TFEA). Figure 3 shows the 3% polymer solution viscosity change for polymers of HFBM, in TFEA, with respect to mole% DHS. It is important to note that in contrast to the vinyl fluorocarbon polymers that are generally considered to have poor adhesive properties the low molecular weight polymers of HFBM adhere to glass. As described below, poly(heptafluorobutyl acrylate) is elastomeric and adheres to many substrates including Teflon.

FIGURE 2: REFRACTIVE INDEX OF P(HFBM), P(HxFBM) AND COPOLYMERS

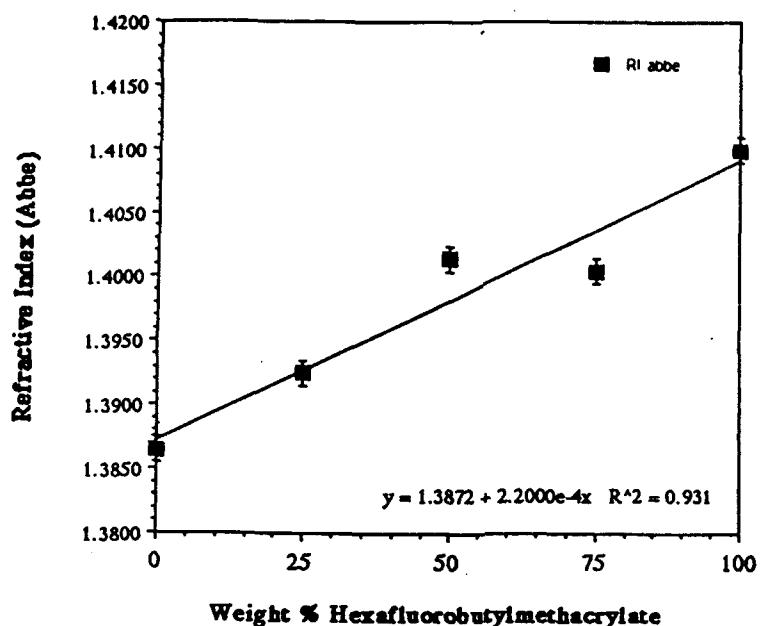
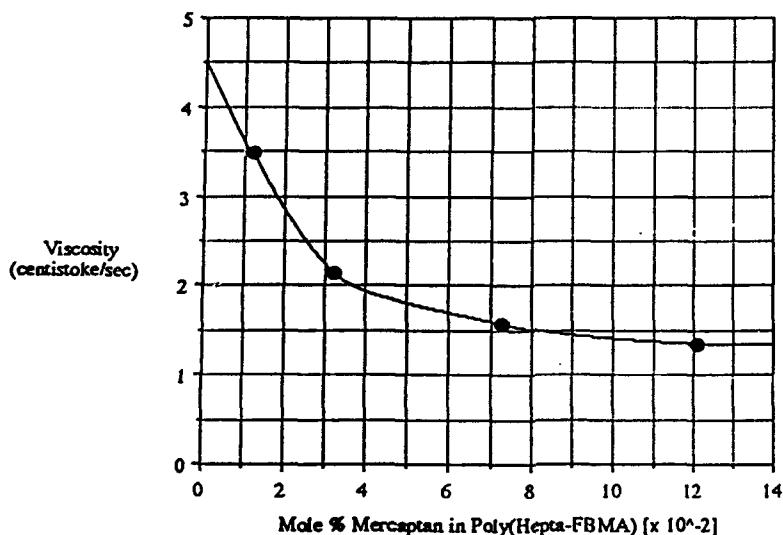


FIGURE 3:



Solution viscosity of 3% poly(hepta-FBMA) in trifluoroacetate versus mole% mercaptan in polymer

3. Emulsion Polymers of HFBM.

Two experimental methods were used to prepare emulsion polymers of HFBM, differing only in the method of addition of the HFBM monomer.

In the first method the monomer was slowly added to a degassed solution of water, surfactant and initiator. This method produced a stable emulsion and the isolated polymer was soluble in TFEA.

In the second method the monomer was added entirely to the water and surfactant then the mixture was degassed and the azo initiator was added. On heating at 50 to 60° for about 10 hrs. some coagulation occurred and the polymer was only partially soluble in TFEA.

It is obvious that each of these methods produce polymers differing in MW. A single attempt to modify the second method, by the addition of the chain growth regulator, DSH, was not successful.

4. Solution Polymerization of HFBM.

Since solutions of P(HFBM) in TFEA were being evaluated for solution coating fibers by The Bicron Corp. it appeared logical to prepare the polymers directly as a solution by polymerization in TFEA. The results of two attempts gave low MW TFEA soluble polymers. An indication of the low degree of polymerization was noted by the solubility of the polymers in acetone. It would appear that either the TFEA is acting as a weak chain terminator or that trace impurities are responsible for the chain termination and consequent low MW polymers. This still appears to be an attractive manufacturing approach. Further work will be done to optimized this process.

B. POLYMER PHYSICAL PROPERTIES.

1. Transparency.

As stated earlier, many commercially available fluorocarbon cladding materials are crystalline or semi-crystalline and not optically clear. P(HFBM) and P(HxFBM) are transparent. This is evidenced in the UV/visible transmission spectra recorded on 10mm thick samples. Figure 4 shows the spectra of homo- and copolymers of HFBM and HxFBM. Even thin films of commercial fluorocarbon cladding polymers are highly opaque(3).

2. Transparency After Irradiation.

The polymers of HFBM and HxFBM are transparent and therefore, very useful for cladding POF's in general. Another, more specific application require that the polymers remain transparent after irradiation. This requirement pertains to use in detectors of high energy radiation.

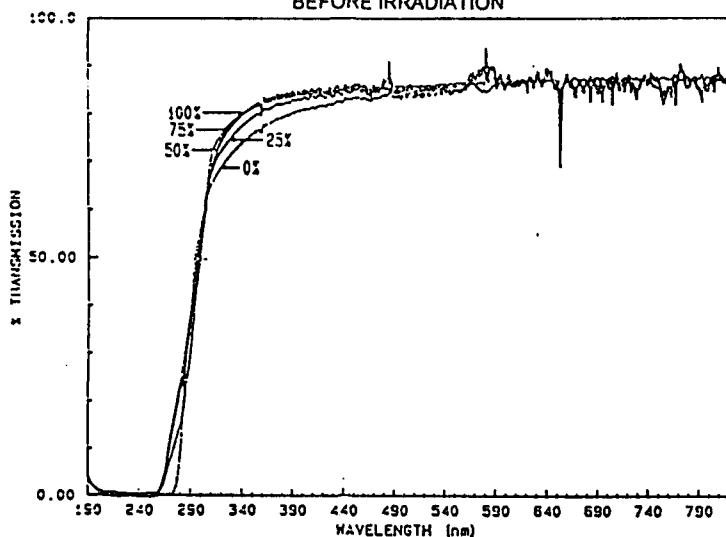
Following the synthesis of bulk polymerized polymers and copolymers of HFBM and HxFBM work was centered on determining the resistance of these polymers toward hard radiation. In order to quantify the optical damage sustained by these polymers, as compared with a PMMA standard, a normalized transmission spectrum was determined between 200 and 800nm before, Figure 4; immediately after, Figure 5; and 7 days following irradiation, Figure 6.

All samples were irradiated at a dose rate of 41 KRad/hr., in a ^{60}Co source to a total dose of 10Mrads. The shift of wave length at 50% transmittance was used, as a point of reference, to compare polymer radiation resistance. Prior to irradiation, all polymers exhibited 50% transmission at a wavelength of about 290nm. A summary of Figures 4-6 is shown in Table 1.

All polymers show some deterioration as evidenced by a non-recoverable 50% transmission shift in wavelength. However, it is apparent when comparing these spectra with that of PMMA, in Figure 7, that the fluorine-containing homo and co-polymers are significantly more resistant to radiation damage than PMMA and P(HFBM) is more radiation resistant than P(HxFBM).

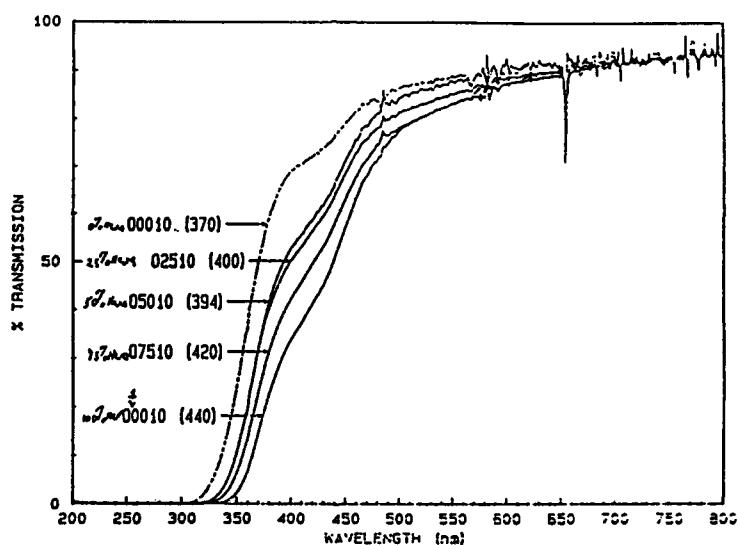
Oxygen permeability, shown in Figure 8, effects the way in which the polymers respond to gamma radiation. Gamma radiation, typically, induces discoloration and the rate of disappearance of color is related to the oxygen permeability of the polymer (4). This is exhibited by the transmission wavelength shift, Figure 5, and the recovery shift, in Figure 6, which is presumed to be due to oxidative changes, through oxygen permeation and reaction of the oxygen with the color body produced by the high energy radiation. Figure 7 shows the comparative radiation resistance of homo and copolymers made from HFBM and HxFBM versus PMMA. Light transmission was monitored through a 14 day period after exposure to a 10 Mrad dose. The P(HFBM) shows the least change after exposure and recovery. The results of these irradiation tests broaden the use of these polymers.

FIGURE 4
P(HFBM), P(HxFBM) AND COPOLYMERS
BEFORE IRRADIATION



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FIGURE 5
P(HFBM), P(HxFBM) AND COPOLYMERS
AFTER 10MRADS IRRADIATION



NOTE: Spikes
in the spectra
at longer
wavelengths are
due to
instrument
error.

FIGURE 6
P(HFBM), P(HxFBM) AND COPOLYMERS
AFTER SEVEN DAYS RECOVERY

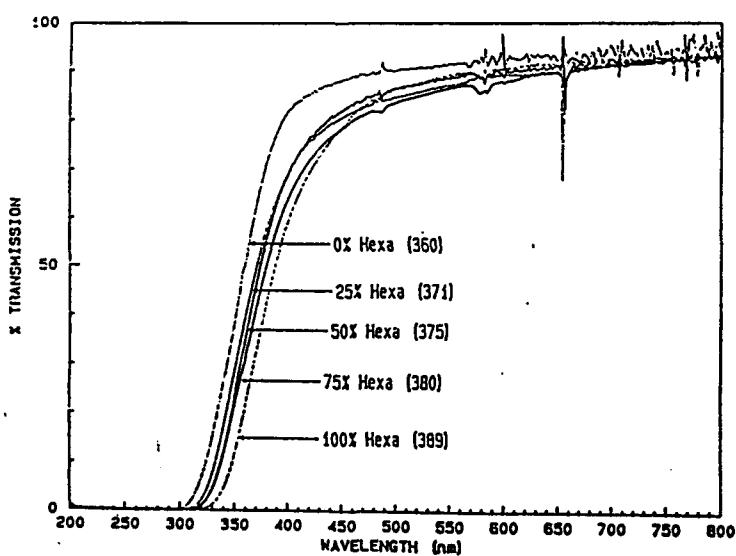


TABLE 1: Effect of 10 MRADS Irradiation on P(HFBM), P(HxFBM) and Copolymers Before and After Seven Days Recovery

Sample ID	Wavelength at 50% Transmission Before Irradiation (nm)	Wavelength at 50% Transmission Right After Irradiation (nm)	Wavelength at 50% Transmission After 7 Days Recovery (nm)
100% hexa / 0% hepta	290	440	389
75% hexa / 25% hepta	290	420	380
50% hexa / 50% hepta	290	394	375
25% hexa / 75% hepta	290	400	371
0% hexa / 100% hepta	290	370	360

FIGURE 7: TRANSMITTANCE RECOVERY AFTER
10MRADS: All samples are 5mm thick, Dose rate at 0.04 Mrads/hr

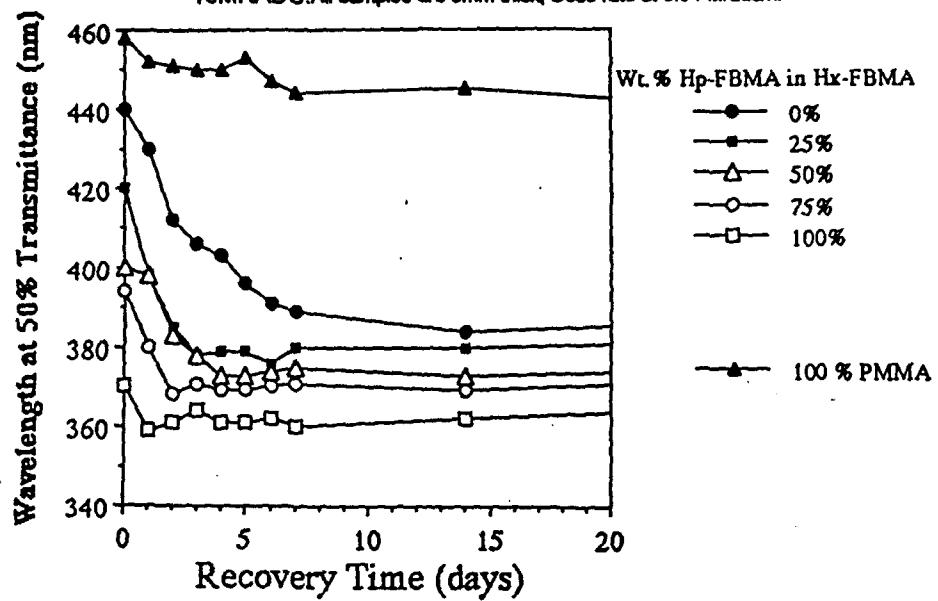
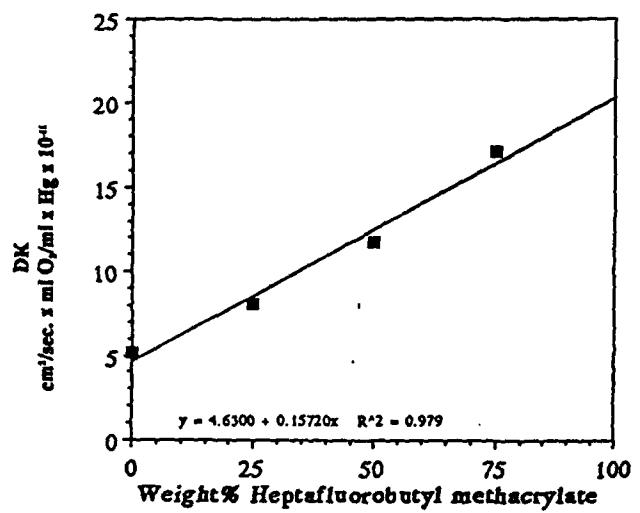


FIGURE 8: Oxygen Permeability, (DK), of P(HFBM),
P(HxFBM) and Copolymers



3. Dynamic Mechanical Analysis (DMA).

DMA of bulk polymerized HFBM was done comparatively with PMMA using molded rectangular bars and run at a fixed frequency of 1Hz and an amplitude of 0.8 mm and a temperature ramp of 2°C/min. The Flexural Storage Modulus and the Flexural Loss Modulus, Figures and 9 and 10 show the onset of softening at a temperature below that of T_g of 65° or at about 50°C. This indicates that these polymers are rigid and self supporting at temperatures up to or near 60°. It also points to the fact that this polymer can be heat processed at temperatures lower than that used to process PMMA. Other commercial fluorocarbon polymers are heat processed at much higher temperatures.

4. Glass Transition (T_g) and Thermal decomposition (T_d)

Temperatures of HFBM and HxFBM Polymers.

Table 2 shows the T_g and T_d of polymers and co-polymers of HFBM and HxFBM. It of interest to note the high and identical decomposition temperatures and the small difference in T_g 's of these polymers.

C. Other Fluorocarbon Methacrylate and Acrylate Polymers.

Some very interesting experimental fluorocarbon acrylate polymers were prepared. In contrast to the somewhat brittle polymers of HFBM, surprisingly, it was found that polymers of heptafluorobutyl acrylate, P(HFBA) have a T_g below room temperature and are optically clear, very tacky, adhesive, elastomeric solids. They adhere tenaciously to many substrates including Teflon. Similarly, polymers of hexafluoroisopropyl acrylate P(HxFIPA) are optically clear, non-tacky elastomeric solids.

Bulk polymerized 2,2,2 trifluoroethyl methacrylate, unlike other polymers in the homologous series, is soluble in TFEA without a need for reducing the MW of the polymer. This polymer may also have some utility as a optical fiber cladding material. The monomer cost is much less than HFBM.

Figure 9:

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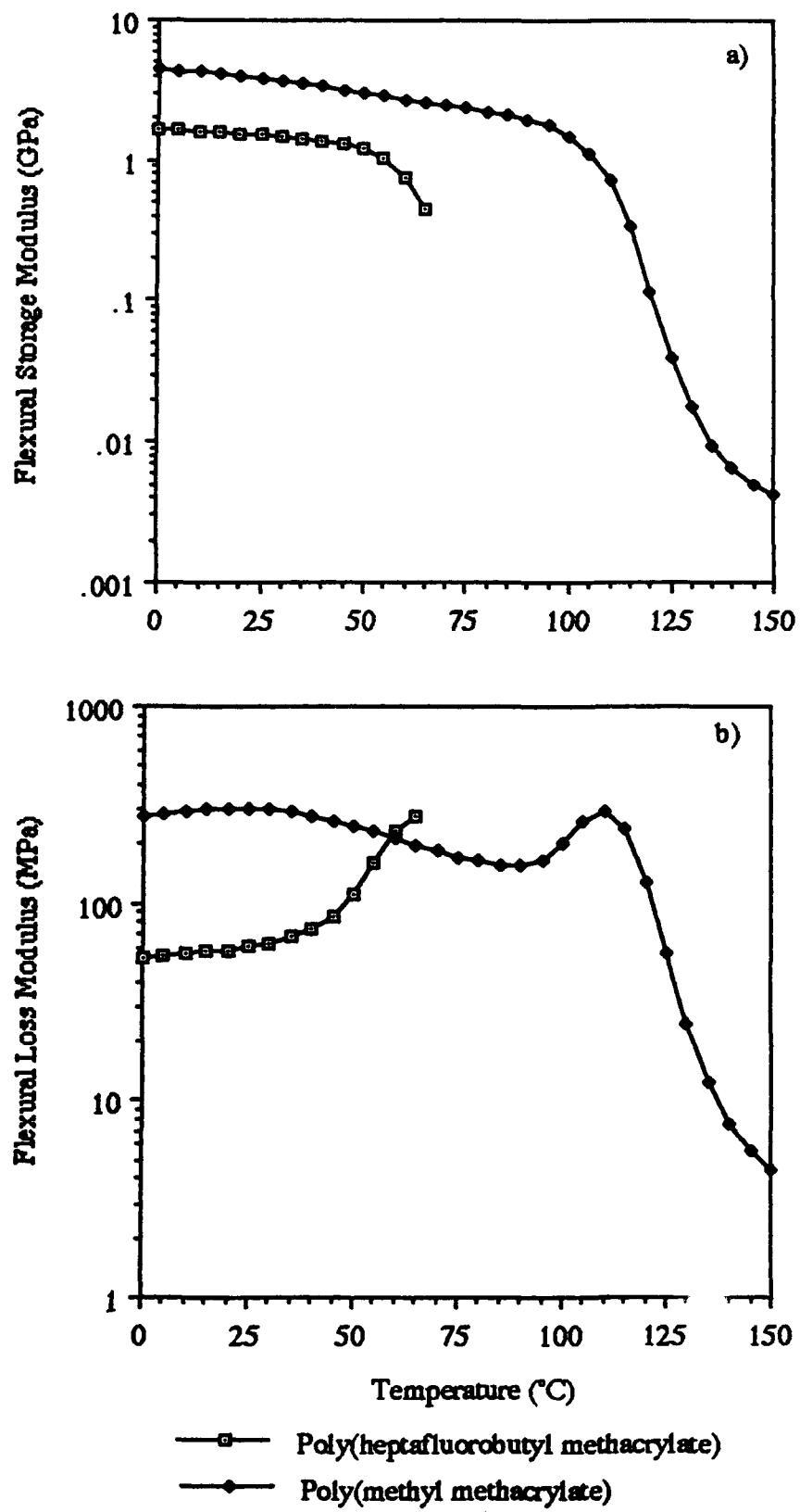


Figure 10: Dynamic mechanical analysis of P(hepta-FBMA) and PMMA
a) Flexural storage modulus and b) Flexural loss modulus
(1 Hz, 0.8 mm amplitude, 2°C/min)

TABLE 2: Glass Transition Temperature and Decomposition Temperature of P(HFBM), P(HxFBM) and Copolymers

Sample ID	T _g (°C)	T _d (°C)
100% hexa / 0% hepta	59	355
75% hexa / 25% hepta	59	355
50% hexa / 50% hepta	57	355
25% hexa / 75% hepta	58	355
0% hexa / 100% hepta	59	355

VI. CONCLUSIONS:

An excellent optical fiber cladding material has been identified, Poly(heptafluorobutyl methacrylate). This is an ideal cladding material that meets all Phase I technical objectives such as: non-crystalline with good optical clarity, low refractive index, stable to hard radiation, has good mechanical properties and is processable at temperatures below that of plastic optical fiber core material.

Polymers of heptafluorobutyl methacrylate have been prepared that are soluble in trifluoroethyl acetate and these solutions have been successfully evaluated by a commercial producer of optical fibers. (Appendix A)

VII. EXPERIMENTAL.

A. Test Methods and Instrumentation.

Tests 1 through 5 were carried out at the U. of Florida. The remaining tests were done at OPRI.

1. UV/Vis Transmission Spectra were determined using a Hewlett Packard Diode Array Spectrometer Model 8452A, wavelength range 200 to 800nm. Samples were compression molded into discs approx. 10 mm thick and 15mm dia.

2. Refractive Index was determined with a Abbe' refractometer. The polymers were compression molded at 100° into approximately 0.3mm films. RI was measured using methylene iodide for good contact.

3. Dynamic Mechanical analysis was determined with a Thermal Analysis DMA 983 as a fixed frequency of 1 Hz, and amplitude of 0.8 mm and at a temperature ramp rate of 2°/min.

4. Thermal Stability was determined on a Thermal Analysis Hi-resolution TGA2950. Heating rate was 20°/min.

5. Glass Transition Temperature, Tg was determined on a Thermal analysis DSC 2910 using a modulated temperature program. Samples were ramped from 0° to 80° at 2°/min.

6. Oxygen Permeability was determined by the Fatt Method (3), on polymer discs, approx 0.2 mm thick using a Createch O₂ Permeometer, model 201T with a Rehder polarographic cell. The disc is placed in a closed cell

over a saline solution saturated tissue paper for electrical conductivity. The units are $\text{cm}^2/\text{sec.} \times \text{ml O}_2/\text{ml} \times \text{mm Hg} \times 10^{-11}$.

7. Viscosity was measured using a Cannon-Fenske viscometer in a water bath at 30° . Viscosity in centistokes.

8. Specific Gravity was determined according to ASTM D792

Method A.

B. Polymer Synthesis.

1. Bulk Polymerization.

a. Unmodified. Bulk polymerization of all fluorocarbon acrylates and methacrylates were carried out as follows:

The fluorocarbon monomers as received from the manufacturer, PCR, Inc., Gainesville Florida, contain a polymerization inhibitor, methoxyhydroquinone, which is removed by washing, several times, with a 5% solution of sodium hydroxide then dried with molecular sieve Type 4A.

To the dried monomer is added 0.2% polymerization catalyst, Vazo 52, 2,2'-azobis(2,4-dimethylvaleronitrile), from E. I. DuPont, Wilmington, Del. The solution is then degassed (removing oxygen) by refluxing under vacuum. The vacuum is brought to atmospheric pressure with nitrogen.

The flask containing the degassed monomer and polymerization containers, (for small samples, typically polypropylene test tubes), are placed in a dry bag and the atmosphere in the dry bag is replaced with nitrogen. The containers are filled with the catalyzed monomer(s), capped, removed from the dry bag and placed in a water bath at 30° for 48 hours, 24 hours at 45° followed by 100° for 2 hours, in an air oven, for a final cure.

b. Modified polymers. Modified polymers were prepared as in (a) by adding docecyld mercaptan before degassing the monomer.

2. Emulsion Polymers.

a. Unmodified emulsion polymers. A Morton flask is charged with distilled water, (89%) a fluorosurfactant, (unidentified, nonionic fluorocarbon surfactant type FSN, from DuPont, Wilmington, Del.), (0.9%), and the mixture heated to reflux while sweeping the system with nitrogen to remove oxygen. The temperature is reduced to 50° and the initiator, V-50, 2,2'-Azobis(2-amidinopropane)dihydrochloride, from Wako Pure Chemicals Industries, Ltd., Richmond, Va., (0.015%) is added, followed by the immediate,

but very slow, addition of the fluorocarbon methacrylate, (10.1%).

This procedure produced a stable emulsion. The emulsion is precipitated by addition to an equal amount of acetone. The precipitated polymer is washed repeatedly with hot water to remove the surfactant, then filtered and oven dried.

b. Modified emulsion procedure. A procedure was run by combining water, surfactant and the fluorocarbon, using the (a) formulation, then degassing the mixture by heating to reflux while purging with nitrogen. After reflux and cooling to 50° the V-50 catalyst was added and the reaction mixture stirred for 16 hours at 50°. This method resulted in a mixture of coagulum and emulsion, samples of each were found to be insoluble in TFEA.

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31 January 1994

Optical Polymer Research, Inc.
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Attn.: Dr. Paul Schuman, President

Dear Paul,

I am writing to report on our experiments with your fluorinated polymers as optical cladding on our plastic scintillating optical fibers.

Your materials definitely represent an improvement over other polymers we have employed in this work. They are the only ones with which we have actually observed improvements in fiber performance. All other materials have required such difficult chemical and physical conditions during the application process that the resultant fibers were always degraded. Hence, we are strongly encouraged with the samples you have sent.

We are using your polymers to apply low refractive index optical claddings to our present fiber by means of fairly standard aftercoating methodology. The coatings are being applied over our present PMMA claddings which are applied by our well-developed precladding technology. There is no doubt, however, that our aftercoating techniques need improvement. I am sure that our own shortcomings are in a large part responsible for the fact that we have not yet come close to achieving theoretical performance with your recent polymer.

With your latest polymer we have improved light output by 10% and have maintained the same attenuation length of our standard fibers. Both results are good news. With refinements in your materials and our process, we look forward to increasing the light output by 50-70%. One would normally expect a worsening of attenuation length as the cladding refractive index is lowered. Consequently, maintenance of the original attenuation length is a very hopeful sign.

It is interesting to note that all of the commercial sources of low refractive index polymers suitable for optical cladding are available only from Japan. We have contacted all of the known Japanese sources and have met with strong resistance (with sincere apologies, of course) to their being able to export such technology to the US. Clearly we need a reliable domestic source for such materials. We look forward to continued collaboration with you in this work.

Very truly yours,

Charles R. Hurlbut
Manager, Organic Scintillator Technology